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(19)

(54) DRY LIGHT-WEIGHT CEMENT COMPOSITIONS, AND COMPOSITIONS FOR MIXING WITH CEMENT TO FORM SUCH CEMENT COMPOSITIONS

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, dc hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a dry light-weight cement composition suitable for use in an underground borehole, and with a composition suitable for mixing with cement to form such a dry light-weight cement composition. Underground boreholes are used for producing oil, water, gas and any other valuable products from underground formations.

When drilling an underground borehole into subsurface formations it is necessary from time to time to insert casing over at least part of the borehole and to cement this casing to the formation. For this purpose an aqueous cement slurry is pumped through the casing that is suspended in the borehole, after which the slurry with the mud following the slurry is pressed upwards through the annular space around the casing.

The pumping pressure under which the slurry is passed through the casing should be sufficiently high to overcome the frictional resistance which the slurry and the mud meet in the casing and the annular space. In the case of deep wells, however, the pressure in the cement slurry will often exceed the fracturing pressure of the formation, as a result of which the formation will break and slurry and/or mud will get lost in the formation. The same will be likely to occur in offshore wells where as a result of the difference in density between the column of sea water and the column of cement slurry of the same height, the pressure of cement at the bottom of the well is often higher than the formation fracturing pressure. In order to solve this problem it has already been proposed to reduce the density of the cement slurry by adding a filling agent consisting of bitumen particles thereto.

To prevent the decrease in strength of the cement after hardening, which decrease results from the addition of bitumen to the cement composition, it has already been proposed to add an aluminium silicate-containing strengthening agent (pozzuolana) to the composition.

It has been found, however, that known light-weight cement compositions comprising a bituminous filling agent and "pozzuolana" do not meet the requirements set by the conditions met during the drilling operations that are nowadays carried out. These conditions require on the one hand an extremely small density of the cement slurry in order to prevent fracturing of the formation facing the borehole or well that is to be cemented, and on the other hand require a high compressive strength of the hardened cement.

It has now been found that these conflicting objectives can be met by the cement composition of the present invention. A further advantage thereof is that during transport of the dry composition there is no risk of gravity separation of the components thereof which would require remixing of the composition prior to adding the required amount of water thereto to form the cement slurry. Another advantage is that the bitumen filling agent is not liable to sticking, thereby allowing an easy transport of the dry light-weight composition from the manufacturing plant to the drilling field over very long distances and time periods, and under high temperature conditions.

According to the present invention a dry light-weight cement composition suitable for use in an underground borehole, com-

prises at least cement, a powdered bituminous filling agent and a particulate aluminium silicate, the powdered bituminous filling agent being formed from a bitumen obtained by precipitating a residual crude oil fraction and having over 90%, by weight, of its particles smaller than 700 microns, and more than 90%, by weight, of the particles of aluminium silicate having a diameter less than 30 microns.

Also, according to the present invention a composition suitable for mixing with cement to form a dry light-weight cement composition as defined above, comprises at least a bituminous powder and particulate aluminium silicate, wherein the bituminous powder has been formed from bitumen obtained by precipitating a residual crude oil fraction, over 90%, by weight, of the particles of the bituminous powder being smaller than 700 microns, and more than 90%, by weight, of the particles of the aluminium silicate having a diameter less than 30 microns.

By this combination of particle sizes, a cement composition is obtained which can withstand severe transport conditions during which the composition is subjected to vibrations without showing any separation of the components thereof and/or subjected to pressure and/or heat without showing any sticking of the bitumen particles. Moreover, the composition shows a very desirable low density, without sacrificing, however, the compressive strength of the composition after hardening thereof. At least 50%, by weight, of the bitumen particles of a dry light-weight cement composition according to the invention, may be smaller than 250 microns. Also, all bitumen particles may be smaller than 500 microns and have an average size of 170 microns.

The bitumen used in the present composition is not noxious to the health of the people handling the bitumen since it is obtained by precipitation of residual crude oil fractions ie. the residual fractions obtained in the distillation of crude oil or shale oil as well as the components obtained from those fractions and the residues obtained by distilling oils which have been obtained from crude oil by means of technical processes, such as thermal or catalytic cracking processes. A heavy lubricating oil is distilled off from a crude oil or from a fraction obtained from it by a certain treatment, generally at atmospheric or reduced pressure, after which the bitumen is obtained as a residual fraction.

By means of precipitation, i.e., treatment with a precipitating agent (a selective solvent for the lighter components of the bitumens), the so-called precipitation bitumen is obtained from these bitumens. Very suitable precipitating agents are propane and butane. The reason why the bitumens obtained by precipitation are so excellently suitable to be powdered is probably that the lighter components have substantially been removed, so that the precipitation bitumens naturally show less tendency to adhesion.

The precipitation bitumen may be a blown precipitation bitumen which has the advantage of great hardness of the particles produced therefrom. By "blown" bitumen is understood the bitumen obtained by passing oxygen-containing gas (such as air) at elevated temperature through molten bitumen. Certain components of the bitumen are then wholly or partly oxidized in the appropriate places in the molecules. Blowing may be applied in combination with a precipitating treatment either before or after precipitation.

The powdered bituminous filling agent may be formed by grinding bitumen lumps or by atomizing molten bitumen.

At least 95%, by weight, of the aluminium silicate used in dry light-weight cement compositions according to the invention may be smaller than 5 microns. Also, at least 80%, by weight, of the particles of the aluminium silicate may be smaller than 1000 Å.

The weight ratio SiO_2/Al_2O_3 of the aluminium silicate may be equal to 1.

The aluminium silicate component may be in the crystalline form (zeolites), which may consist of spent catalyst or molecular sieve used in the oil, petrochemical or chemical industries. Also, the aluminium silicate may be in admixture with a proportion of free aluminium oxide and/or silicon oxide, and it may be obtained through precipitation by adding an aluminium compound or a solution thereof to a solution of a silicate. The particles of aluminium silicate may be in the form of agglomerates of smaller particles firmly bonded together, and in such case the herein defined particle sizes refer to such agglomerates.

The dry light-weight cement composition may comprise 0.5-2.0 parts, by weight, of cement and less than 0.2 part, by weight, of aluminium silicate per 1 part, by weight, of powdered bitumen.

The invention will now be illustrated with reference to the following examples.

A blown Qatar Marine propane bitumen, i.e., a bitumen derived from a crude oil from wells penetrating the sea bottom near Qatar and obtained by means of a precipitation treatment of a residual fraction of this crude oil, followed by blowing the so-obtained bitumen with air, was powdered by grinding in a semi-commercial grinder. In this way about 10 tons were obtained of a bitumen powder with a softening point (Ball and Ring) of 120°C and such a distribution of

particle size that 100% of the particles was smaller than 500 microns, 80%, by weight, of the powder was formed by particles smaller than 300 microns, 60%, by weight, of the powder was formed by particles smaller than 200 microns, 20%, by weight, of the powder was formed by particles smaller than 100 microns and 10%, by weight, of the powder was formed by particles smaller than 70 microns. The average size of the particles of this bitumen powder was 170 microns. The powdered bitumen accordingly met the particle size requirement of the present invention. 5%, by weight, of aluminium silicate powder was added to these 10 tons of bitumen powder. 95%, by weight, of the aluminium silicate powder had a particle size of less than 5 microns. The density was 2.15 and the specific surface was about 120 m²/gram.

The 10 tons of bitumen powder were thoroughly mixed with the aluminium silicate powder and thereafter transported over a substantial distance in a cement bulk carrier. No detrimental caking of the particles took place during this transport since the aluminium silicate powder acted as an anti-caking agent.

Subsequently, the mixture of bitumen powder and aluminium silicate powder was mixed by fluidization by means of air with 10 tons of oil-well cement of a type known under the commercial indication of "API class G". The pneumatic transport both of the mixture of bitumen and aluminium silicate powder immediately before mixing with the cement and of the final mixture of bitumen/aluminium silicate/cement did not present any difficulties regarding caking of particles or separation thereof, notwithstanding the fact that the density of the oil-well cement (3.2 grams/cm³) was considerably higher than that of the bitumen powder (1.0 gram/cm³).

The cement composition was subsequently mixed with the appropriate amount of water to form a pumpable slurry, which slurry was pumped through a cement string down into the hole to a level where the casing was to be cemented. The slurry entered the annular space around the casing and was retained therein to harden.

Based on the bitumen/aluminium silicate powder mixture prepared as described above, various mixtures were prepared with varying percentages of aluminium silicate with a weight ratio of cement/bitumen of 1.25 and a weight ratio of water/cement of 1.24. Provisions were made to ensure that each time the density of the fresh cement slurry was 1.3 g/cm³.

The aluminium silicate had a double function, firstly to minimize the risk of caking of the particles of the bitumen powder, and secondly to increase the compressive strength of cement to which bitumen powder has been added for decreasing the density thereof.

The compressive strength of all mixtures was determined in special experimental samples of the cement slurry during 24 hours after hardening at a temperature of 20°C. However, for each mixture the temperature at which hardening took place was kept at three different values in different experimental samples, namely: 32°C, 43°C and 78°C.

The results of the measurements are incorporated in the graph shown in the drawing. In this graph the compressive strength of the hardened cement is indicated in kg/cm² and plotted against the content of aluminium silicate in a weight percentage. Three areas have been indicated in the graph for the three hardening temperatures mentioned above. The graph clearly shows that the addition of aluminium silicate has a positive influence on the compressive strength of the oil-well cement for each hardening temperature. It has also been found that a rise in the temperature at which hardening takes place will bring about an increase of the compressive strength.

The importance of the influence of the temperature on the strength after the hardening of the cement becomes clear when it is considered that the temperature in the borehole increases with its depth.

By way of comparison another batch of bitumen of the same type as described above, was ground in a commercial grinder, whereby 4 tons of bitumen powder were obtained with a particle size distribution such that 100%, by weight, of the particles was smaller than 2000 microns, and 90%, by weight, of the powder was smaller than 1000 microns. The average particle size was about 250 microns. Such powdered bitumen did not, therefore, meet the requirements of the present invention in regard to particle size. The bitumen powder was subsequently mixed with 5% (by weight) of aluminium silicate (having a particle size less than 30 microns) and 5 tons of Pozmix cement. Although no problems were encountered with mixing and pneumatic transport of the mixture with respect to caking and separation of bitumen/cement/aluminium silicate mixture, when various cement slurries with a water/cement ratio of 0.6 - 0.7 were tested, the compressive strength of these slurry samples was found to be below the requirement of 35 kg/cm² under standard conditions.

By replacing the 10%, by weight, of coarse bitumen particles, i.e. the 10% of particles having a size greater than 1000 microns, by the same weight of particles of a size smaller than 1000 microns such that the resulting powdered bitumen contained 95%, by weight, of particles smaller

than 700 microns, compressive strengths over 35 kg/cm^2 at the same conditions were found. The particle distribution of the powdered bituminous filling agent was the following:

100%, by weight : $d < 1000\ \mu$
95%, by weight : $d < 700\ \mu$
75%, by weight : $d < 500\ \mu$

The average diameter d_{50} was slightly less than 250 microns.

It will be appreciated that the invention is not limited to the examples described above.

If desired, the bitumen powder may be mixed together with the cement and the strengthening agent instead of first mixing the bitumen powder with the strengthening agent followed by mixing the mixture thus obtained with cement.

The particle size of the bitumen powder must be such that over 90%, by weight, of the particles is smaller than 700 microns. Good results are obtained when using such a bitumen powder in which over 50%, by weight, of the particles is smaller than 250 microns.

Further, the invention is not limited to the application of an aluminium silicate having the particle size mentioned in the examples described above. Good results are obtained by using aluminium silicate having over 95%, by weight, of the particles with a diameter less than 5 microns. Extremely good results may be expected, however, when using aluminium silicate of which at least 80%, by weight, of the particles is smaller than 1000 Å.

In an alternative embodiment of the invention, the aluminium silicate and/or the cement is added to the bitumen during the manufacture of the bitumen powder. In general, it can be said that in the method of preparing a dry light-weight cement composition according to the invention, the powdered bituminous filling agent is mixed during or after the manufacture thereof with at least a part of at least one of the other components of the composition, and in practice it is advantageous when admixture is effected after manufacture of the powdered bituminous filling agent to do so as soon as practicable thereafter.

WHAT WE CLAIM IS:

1. A dry light-weight cement composition suitable for use in an underground borehole, comprising at least cement, a powdered bituminous filling agent and a particulate aluminium silicate, the powdered bituminous filling agent being formed from a bitumen obtained by precipitating a residual crude oil fraction and having over 90%, by weight, of its particles smaller than 700 microns, and more than 90%, by weight, of the particles of the aluminium silicate having a diameter less than 30 microns.

2. A cement composition according to claim 1, wherein at least 50%, by weight, of the powdered bituminous filling agent particles is smaller than 250 microns.

3. A cement composition according to claim 1 or 2, wherein the particles of the powdered bituminous filling agent are smaller than 500 microns and have an average size of 170 microns.

4. A cement composition according to any one of claims 1-3, wherein the powdered bituminous filling agent consists of blown bitumen.

5. A cement composition according to any one of claims 1-4, wherein the powdered bituminous filling agent is formed by grinding bitumen lumps.

6. Cement composition according to any one of the claims 1-4, wherein the powdered bituminous filling agent is formed by atomizing molten bitumen.

7. A cement composition according to any one of claims 1-6, wherein at least 95%, by weight, of the aluminium silicate particles is smaller than 5 microns.

8. A cement composition according to any one of claims 1-7, wherein at least 80%, by weight, of the aluminium silicate particles is smaller than 1000 Å.

9. A cement composition according to any one of claims 1-8, wherein the weight ratio: SiO_2/Al_2O_3 of the aluminium silicate is equal to 1.

10. A cement composition according to any one of claims 1-9, wherein the aluminium silicate comprises one or more zeolites.

11. A cement composition according to claim 10, wherein the zeolites consist of spent catalyst or molecular sieve used in the oil, petrochemical or chemical industries.

12. A cement composition according to any one of claims 1-9, wherein the aluminium silicate has been obtained through precipitation by adding an aluminium compound or a solution thereof to a solution of a silicate.

13. A cement composition according to any one of claims 1-12, comprising 0.5 - 2.0 parts, by weight, of cement and less than 0.2 part, by weight, of aluminium silicate per 1 part by weight of powdered bituminous filling agent.

14. A dry light-weight cement composition as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the examples.

15. A method of cementing an underground borehole, wherein an aqueous cement slurry is pumped down into the borehole, the slurry being prepared by mixing the dry light-weight cement composition according to any one of the claims 1-14 with water.

16. A method of preparing a dry light-weight cement composition according to any one of the claims 1-14, wherein the powdered bituminous filling agent is mixed during the manufacture thereof with at least a part of at least one of the other components of the composition.

17. A composition suitable for mixing with cement to form a dry light-weight cement composition as claimed in claim 1, comprising at least a bituminous powder and particulate aluminium silicate, wherein the bituminous powder has been formed from bitumen obtained by precipitating a residual crude oil fraction, over 90%, by weight, of the particles of the bituminous powder being smaller than 700 microns, and more than 90%, by weight, of the particles of the aluminium silicate having a diameter less than 30 microns.

18. A composition according to claim 17, wherein at least 50%, by weight, of the particles of the bituminous powder is smaller than 250 microns.

19. A composition according to claim 17 or claim 18, wherein the particles of the bituminous powder are smaller than 500 microns and have an average size of 170 microns.

20. A composition according to any one of claims 17-19, wherein at least 95%, by weight, of the aluminium silicate particles is smaller than 5 microns.

21. A composition according to any one of the claims 17-20, wherein at least 80%, by weight, of the aluminium silicate particles is smaller than 1000 Å.

22. A cement composition according to any one of the claims 17-21, wherein the SiO_2/Al_2O_3 weight ratio of the aluminium silicate is equal to 1.

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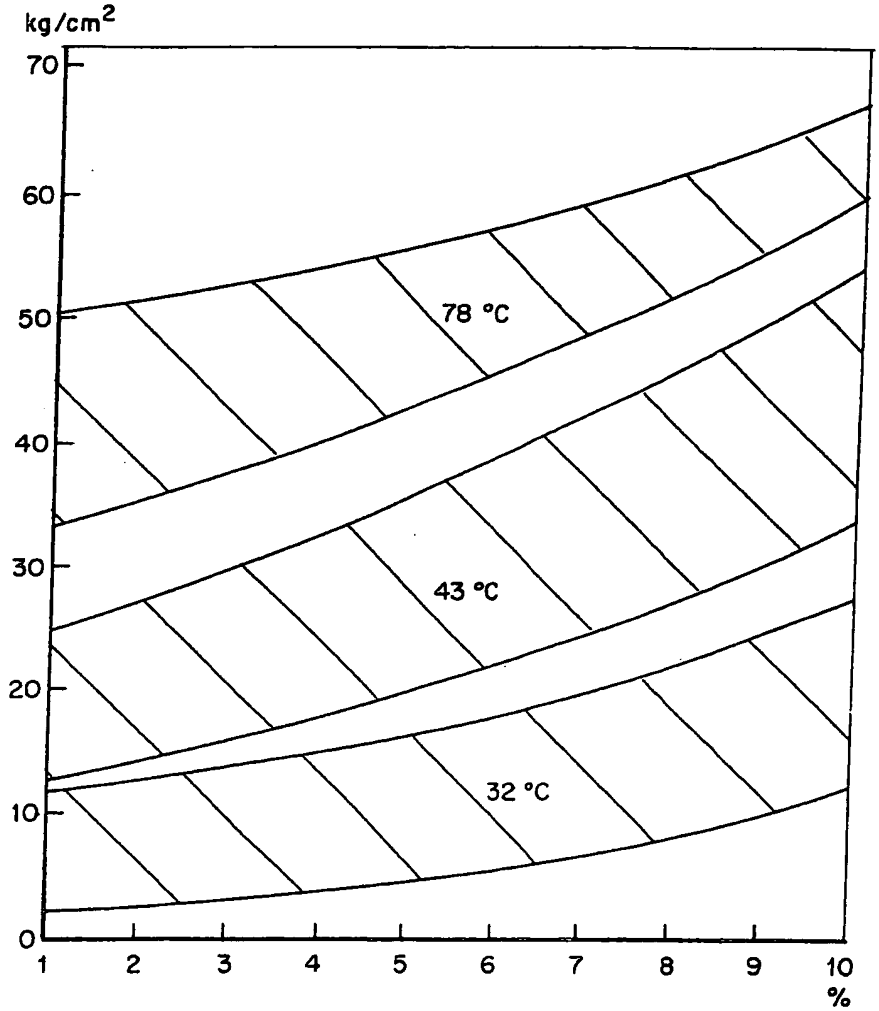
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